CORROSION RESISTANCE OF NEW TiMo ALLOYS FOR BIOMEDICAL APPLICATIONS

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In this paper are shown experimental results regarding the corrosion behavior in simulated physiological solution on four alloys TiMo, with 5% Mo, 7% Mo, 11% Mo, respectively 12% Mo. Structural investigations have revealed a dual-phase structure, which contains α'' martensite and β phase, in proportions depending on the molybdenum content. The corrosion resistances of the alloys were tested in NaCl infusion solution and Ringer solution. Regardless of the type of the test solution it was noticed that the corrosion potential shifted to a more electropositive value, corrosion current densities and corrosion rates have dropped with the augmentation of molybdenum content.

Keywords: titanium molybdenum alloys, β solution, α''martensite, corrosion resistance

1. Introduction

The metallic materials that hip joint implants are made of should not produce physiological reactions to the surrounding tissues. Interaction between implant and tissues around implant should not cause corrosion, biodegradation of the surface, organic changes or a secondary instability of biological implant. Biomedical titanium and its alloys are considered to be the best metallic materials for orthopedic applications. Intrinsic properties of these types of materials provide: high mechanical resistance, low modulus of elasticity, corrosion resistance, high biocompatibility and non-toxicity. In the last few years [1÷23], Ti-Mo alloys as biomaterials have been studied, emphasizing the microstructure, their mechanical properties, the wear resistance and corrosion properties or cytotoxicity.

This work proposes for investigation new titanium alloys with molybdenum contents in the range of 5÷12% in order to put in evidence the structural characteristics and corrosion resistance in two physiological fluids.

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2. Materials and Experimental Procedures

Elaboration of the experimental alloys was made by RAV technology, with the chemical composition given in Table 1.

Table 1.

Chemical composition of the experimental Titanium-Molybdenum alloys

Alloy	Chemical Composition, %wt.									
	Ti	Mo	Al	C	Fe	Mn	Ni	Pd	Si	Sn
Ti5Mo	93.6	5.16	0.0067	0.015	0.033	0.015	0.029	0.018	0.0054	0.85
Ti7Mo	92.4	6.98	0.023	0.016	0.050	0.021	0.014	0.021	0.012	1.09
Ti11Mo	87.2	10.98	0.025	0.016	0.038	0.017	0.016	0.033	0.025	1.48
Ti12Mo	86.5	11.94	0.0037	0.014	0.028	0.016	0.020	0.034	0.023	1.46

Specific samples were made from titanium alloys ingots for microstructural characteristics determination by metallographic analysis, X-Ray diffraction and scanning electron microscopy. Corrosion resistance tests were performed by drawing the potentiodynamic polarization curves on potentiostat-galvanostat AUTOLAB, PGSTAT302N, equipped with NOVA 1.4 soft, on cylindrical samples Φ5 x 1 (mm), after special preparation (sampling, grinding, polishing). Two physiological solutions were selected for electrochemical experiments:

- NaCl infusion solution, which consists in NaCl 0.9% m/v, respectively sodium chloride (9g) and water up to 1000 ml of infusion solution,
- Ringer solution, which consists in: potassium chloride (0.40g); calcium chloride dehydrate (0.27g); sodium chloride (6.00g); sodium lactate (3.17g); rest water up to 1000ml.

3. Results and Discussion

The phase constitution of the TiMo experimental alloys was identified by metallographic analysis and X-ray diffraction analysis. Microstructural aspects of the experimental alloys after the qualitative and quantitative optic metallographic analysis are given in Fig. 1, showing a martensitic phase and a solid solution. One may observe that X-rays diffraction analysis (Fig.2) reveals the martensitic phase as orthorhombic α'' martensite near β solid solution phase.

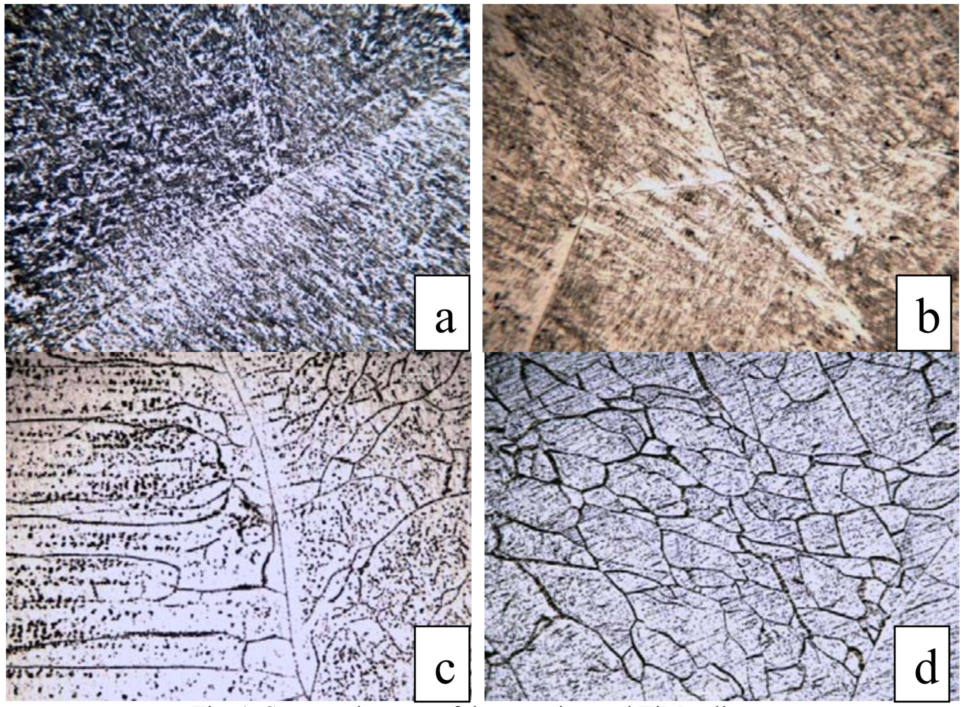


Fig. 1. Structural aspect of the experimental TiMo alloys:
(a) alloy Ti5Mo , (b) alloy Ti7Mo, (c) alloy Ti11Mo, (d) aloy Ti12Mo

Metallographic analysis shows that Ti5Mo and Ti7Mo have dual phase structure, consisting in a high proportion of orthorhombic α'' martensite and a small proportion of β solid solution. At higher contents of molybdenum, respectively for Ti11Mo and Ti12Mo alloys, the proportion of the β solid solution increases, without elimination of orthorhombic martensite.

The results are in accordance with the references and Ho [1], which studied a large field of molybdenum contents in titanium alloys, observed that the presence of the orthorhombic martensite may begin at 7.5%Mo.

In another recent paper, Ho [2] showed the structural modifications due to the molybdenum content, in Ti-5Cr alloys. Lin [3-4] investigated the alloys group from the Ti-7.5Mo-Fe system, defining the orthorhombic martensite near to a small proportion of ϖ phase, that gives a hardening effect.

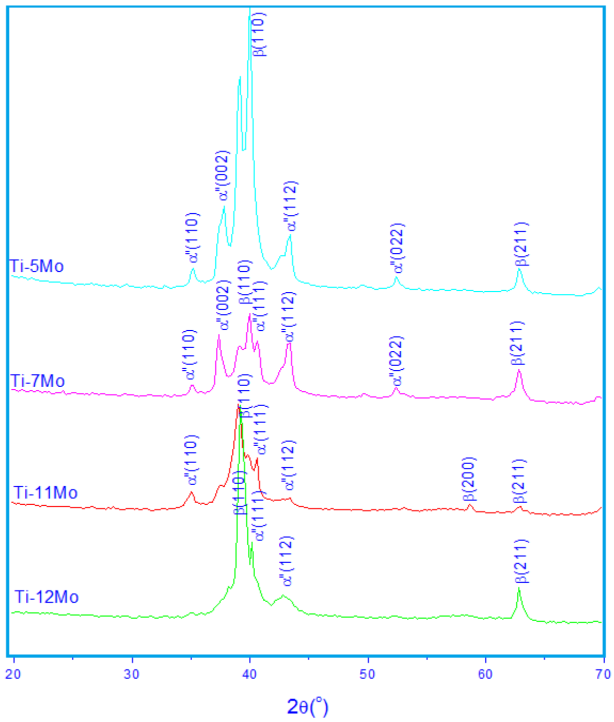
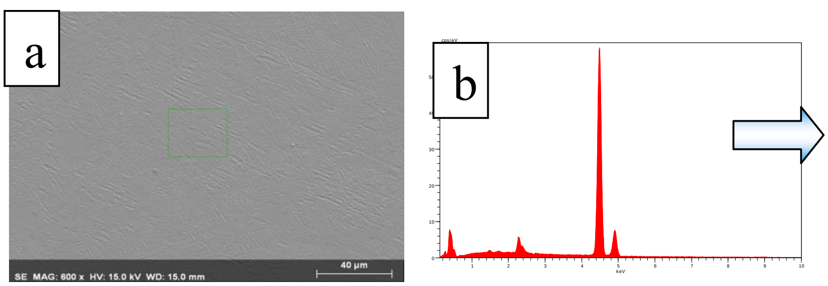
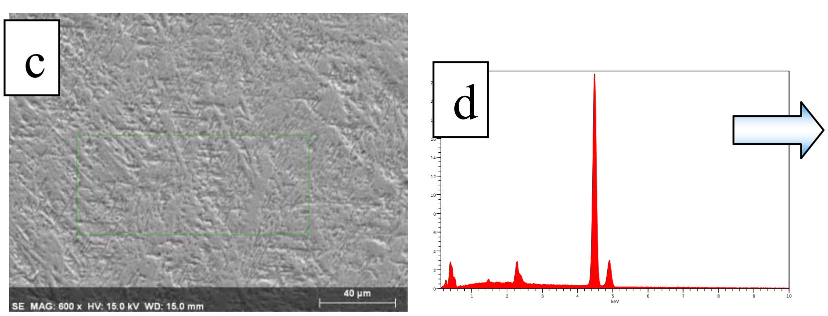


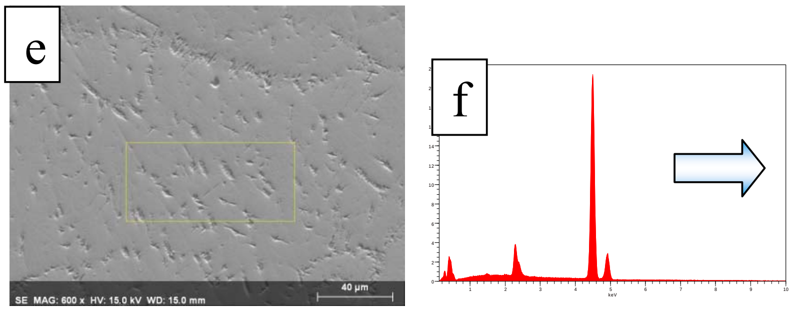
Fig. 2- X-rays diffraction pattern of the experimental TiMo alloys



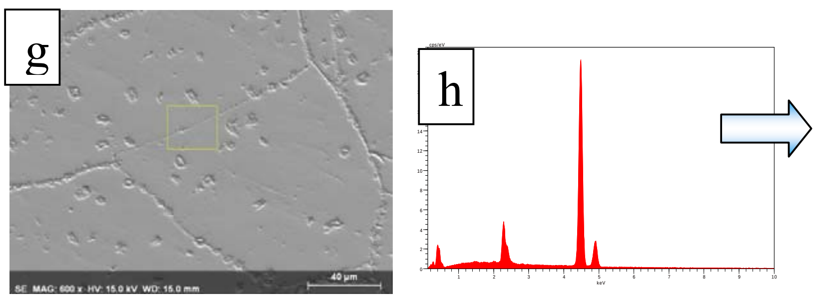
Local microcomposition, %wt	
Ti	Mo
94.62	5.38



Local microcomposition, %wt	
Ti	Mo
92.77	7.23



Local microcomposition, %wt	
Ti	Mo
88.34	10.42



Local microcomposition, %wt	
Ti	Mo
87.85	12.15

Fig. 3. SEM images (a, c, e, g) and EDAX local microcomposition (b, d, f, h)

Chen [5] investigated four alloys of the Ti-Mo system, but with other proportions than those from the present paper, respectively 5%, 10%, 15% and 20%, the Ti-20Mo alloys for dental applications. Wu [6] made some structural correlations for the alloys from the system Ti-Mo-H (with the molybdenum content up to 15%). Gordin [7] studied the structural modifications of two alloys, respectively Ti-8Mo and Ti-16Mo (nitrided at 1400°C), where nitrides were put in evidence either in α solid solution or in β solid solution. Gabriel [8] suggested a new alloy for biomedical applications, respectively Ti-12Mo-3Nb exhibiting only one phase β. Zhou [9] studied the properties of two alloys, Ti-10Mo and Ti-20Mo, after cold forming and heat treatment, proposing the alloy with 10% Mo as a biomedical alloy among other β Ti-Mo alloys. Li [10] brought in for biomedical applications β structure alloys from the system Ti-Mo-Si processed through powder metallurgy, due to a very good combination between high fracture strength, low modulus of elasticity, a large field of forming degree (over 21.5%) and a very good biocompatibility. Almeida [11] studied the alloys from the system Ti-Mo, processed through laser technology, proposing for orthopaedic applications the alloy with 13% Mo, with a low modulus of elasticity (75GPa) and a hardness about 240VHN.

Structural analysis was also made by scanning electron microscopy and presented in Fig. 3. Also, these results are in accordance with optical metallography and X-Rays diffraction analysis, certifying the proposed designed chemical composition, resulted from the spectroscopic analysis. Results on experimental alloys tested in physiological body fluids are given in Fig. 4 and Table 2. One may remark that in NaCl solution the corrosion potential shifts at higher electropositive values, respectively from -187mV (for the Ti5Mo alloy), at -177mV (for the Ti7Mo alloy), then to -70mV (Ti11Mo alloy), reaching a positive value of +79 mV (for the Ti12Mo alloy). In the same manner the corrosion values and corrosion rates fall, respectively $1.99*10^{-3}$μA/cm^2 (Ti5Mo alloy), $1.13*10^{-3}$μA/cm^2 (Ti7Mo alloy), $5.89*10^{-5}$ μA/cm^2 (Ti11Mo alloy), having the lowest value to the highest molybdenum content alloy $3.16*10^{-6}$ μA/cm^2 (Ti12Mo alloy). Also, the corrosion rate that is related with the corrosion current density, decreases from 40.36 μm/year (on Ti5Mo alloy), 22.9 μm/year (on Ti7Mo alloy), 11.93 μm/year (on Ti11Mo alloy), and reaching 0.067 μm/year (on Ti12Mo alloy). It can thus be concluded that in this testing environment, molybdenum has a positive effect, i.e. the corrosion potential move to higher electropositive values and may determine the diminution of the corrosion density currents and decrease of the corrosion rates up to a very small value, 0,067 μm/year, as given in Fig. 4 a.

For the experimental alloys tested in Ringer solution one may remark the displacement of the corrosion potential from the value -188mV (at the $TiMo_5$ alloy), -177mV (at the $TiMo_7$ alloy), -90mV (at the $TiMo_{11}$ alloy) reaching the value of -80mV (at the $TiMo_{12}$ alloy). Also corrosion density values fall from 1.16. 10^{-3} μA/cm^2 ($TiMo^5$ alloy), at 2,01.10^{-4} μA/cm^2 ($TiMo_7$ alloy), 8.84.10^{-3} μA/cm^2 ($TiMo_{11}$ alloy) and respectively 3.71.10^{-5} μA/cm^2 ($TiMo_{12}$ alloy). In the same way, corrosion rate values are from 23.45 μm/year (at $TiMo_5$ alloy), 4.63 μm/year (at $TiMo_7$ alloy), 1.66 mm/year (at $TiMo_{11}$ alloy), up to 0.75 mm per year (at $TiMo_{12}$ alloy).

In comparison with the behavior of the alloys in NaCl solution, the corrosion parameter values in Ringer solutions may be evaluated roughly similar, with the exception of the $TiMo_{12}$ alloy with a positive value of the corrosion potential and a corrosion current very low as compared with the other alloys. It is to be noticed also when testing in the Ringer solution that molybdenum may improve the corrosion resistance by moving the corrosion potential to higher electropositive values, decreasing the corrosion density and corrosion rate. The corrosion rate depending on the alloy type in the tested physiological fluids is shown in Fig. 5.

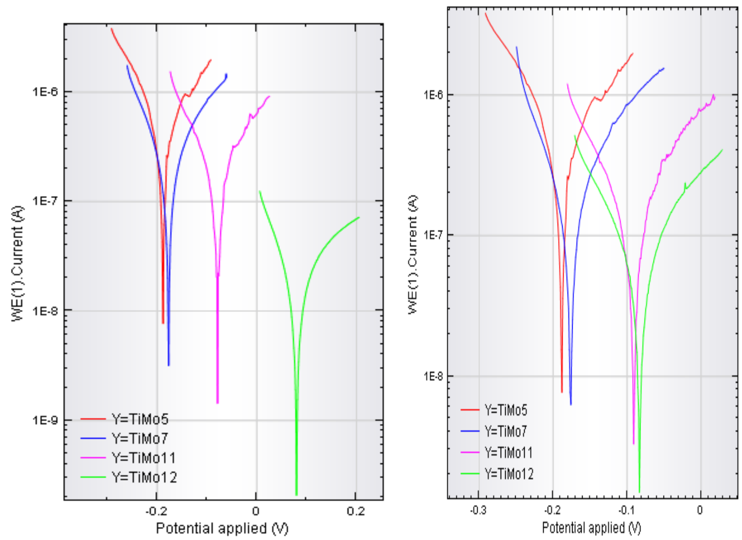


Fig. 4- Potentiodynamic polarization curves of the experimental alloys in NaCl infusion solution (a) and Ringer solution (b)

Table 2

Corrosion parameters and results concerning Tafel slope for the experimental alloys TiMo after corrosion tests in physiological fluids

Alloy	Corrosion					Tafel slope		
	E_{corr} [mV]	i_{corr}, [μA]	R_p [Ohm]	I_{corr} [μA/cm^2]	Corrosion rate [μm/an]	bc [V/dec]	ba [V/dec]	character
NaCl infusion solution								
Ti5Mo	-187	$5.58*10^{-4}$	40,034	$1.99*10^{-3}$	40.36	0.010	0.016	Catodic
Ti7Mo$_7$	-177	$3.18*10^{-4}$	93,189	$1.13*10^{-3}$	22.90	0.016	0.014	anodic
Ti11Mo	-70	$1.65*10^{-4}$	119,440	$5.89*10^{-4}$	11.93	0.013	0.014	Catodic
Ti12Mo	+79	$1.27*10^{-6}$	1,780,900	$3.16*10^{-6}$	0.067	0.010	0.010	mixt
Ringer solution								
$TiMo_5$	-188	$5.61*10^{-5}$	62,118	$1.16*10^{-3}$	23.45	0.017	0.015	anodic
$TiMo_7$	-177	$3.24*10^{-4}$	98,339	$2.01*10^{-4}$	4.063	0.014	0.017	catodic
$TiMo_{11}$	-90	$2.34*10^{-5}$	212,540	$8.24*10^{-5}$	1.660	0.021	0.024	catodic
$TiMo_{12}$	-80	$1.04*10^{-5}$	440,390	$3.71*10^{-5}$	0.75	0.020	0.021	catodic

A comparison of the present paper results with those obtained in the literature allows some interesting assessments. On one hand, the overall results can be compared with various results of literature; on the other hand the results are new, in the sense that in any other works no such combination of alloys having these chemical compositions tested with these physiological human fluids is to be found.

Hence Ho [2] indicates corrosion potential values between -400mV ÷-200mV, but only for alloys Ti-7.5Mo compared with classic Ti6Al4V alloy, and the tests were done in physiologically fluid. Oliveira [12-14] studied the electrochemical behavior of a set of Ti-Mo alloys curves in the open current circuits in Na_2SO_4 solution and Ringer solution. Comparable results are offered by More [15], but on other alloys, those of the Ti-29Nb-13Ta-4,6Zr system compared with Ti-12,5Mo obtaining corrosion potentials of about 900mV (much more electronegative than ours).

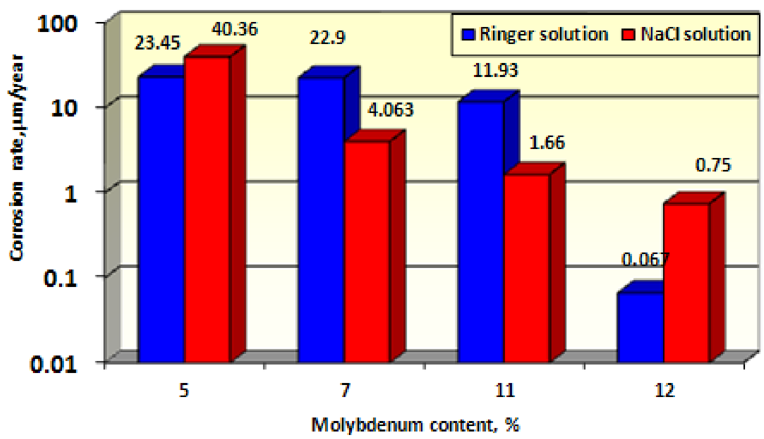


Fig. 5- Influence of molybdenum content on corrosion rates for the experimental alloys after testing in NaCl infusion solution and Ringer solution

Kumar [16] studied the behavior of pure titanium in Ringer solution in order to create a map for phenomena such as corrosion - wear - friction. Gonzales [17] studied the corrosion behavior of titanium alloys as biomaterials for dental applications and concluded that molybdenum may increase the passive film stability, enlarging the passive field due to insoluble molybdenum chloride forming. In other papers [18-20] the corrosion potential for Ti-15Mo alloys has a different behavior of the Ti6Al4V which contain pure titanium and the Ti30Cu10Ag that has different fluorine ions concentration which has a very low potential about -500mV. These authors observed the presence of localized corrosion on the metallic surface. Capela [22] has an interval of corrosion current between -275mV ÷ -457mV, with a density interval of 0.31÷2.3µA/cm2 which may increase with increasing the fluorine ions.

Al-Mayouf [21] studied comparatively the repeatability of the corrosion parameters for TiMo alloys in NaCl solutions, demonstrating the molybdenum beneficial effect by decreasing the corrosion susceptibility in aggressive stimulant human fluids containing 0.9%NaCl. Karthega [23] studied the electrochemical behavior of β alloys in Hank's solution. These authors showed an increased corrosion resistance of the TiMo alloys by forming compact surface layers. Lalik [24] studied the corrosion behavior of welded titanium in hydrochloric acid, putting in evidence localized and general corrosion phenomena, with accelerated corrosion rate.

4. Conclusions

The tested alloys are part of the TiMo system, having 5% Mo, 7% Mo, 11% Mo and 12% Mo; metallographic analysis shows that $TiMo_5$ and $TiMo_7$ have dual phase structure, consisting in a high proportion of orthorhombic α'' martensite and a small proportion of β solid solution. At higher molybdenum contents, respectively for $TiMo_{11}$ and $TiMo_{12}$ alloys, the proportion of the β solid solution increases, without elimination of orthorhombic martensite. The experimental alloys have a good corrosion behavior after testing in physiological human fluids, respectively NaCl solution and Ringer solution. No matter the testing solution, the corrosion potential may shift to bigger electropositive values, the corrosion current density and corrosion rates may decrease with the increasing molybdenum content.

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